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# A Mississippi Flood Control Reservoir: Life Expectancy and Contamination

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### **ABSTRACT**

The fate of reservoirs is a major water management, water quality, and aquatic life use concern across the globe. We examined sedimentation rates, current watershed contamination contributions and potential impacts of long-term row cropping (cotton, corn, soybeans, and sweet potato) in a large flood control reservoir in the loess hills of Mississippi, USA Grenada Reservoir, created in January 1954, was constructed as part of a comprehensive plan for flood control in the Yazoo River Basin in northwestern Mississippi. Two rivers, the Yalobusha and Skuna, contribute inflow to the reservoir, forming a distinctive Y-shape within the topography of the flood pool. Total watershed drainage area for the reservoir is approximately 3,419 square kilometers (1,320 square miles). Reservoir sediment accumulation rates were sampled in 1998 and 1999. Although reservoir life expectancy was originally estimated at 25 years because of high erosion rates in the watershed, our study revealed that the reservoir continues to function with only slightly reduced storage capacity. Sediment accumulation within the permanent pool adjacent to the dam was < 1 cm yr<sup>-1</sup> except for a depositional area near tributary inflow that accumulated sediment at about 5 cm yr<sup>-1</sup>. The central area of the permanent pool experienced sediment accumulation rates that averaged < 1.5 cm yr <sup>1</sup>. Sites within the two reservoir arms fed by the two river inflows showed little or no sedimentation. Sedimentation rates further upstream in these two inflow areas were also generally low. Sedimentation rates within Grenada Reservoir were higher until the mid 1960s & early 70s but were considerably lower thereafter. These lower sedimentation rates paralleled land use changes and followed discontinuance of major upstream channel alterations for flood control. From 1996 to 2002 analyses were conducted in water and sediment for 8 metals and 48 pesticides/ contaminants at 26 stream/river locations and 9 locations within the reservoir. In spite of long-term historical use of residual pesticides in the watershed and widespread use of currently applied agricultural compounds, concentrations in stream or reservoir sediments and overlying water were generally low and sporadic or not detectable Conversely, several metals (arsenic, lead, copper, iron, aluminum and zinc) were abundant in stream and reservoir sediments. Atrazine, a triazine herbicide, was routinely found in stream water and sediment. It was also detected in reservoir water samples but at nearly one fifth less than contributing stream concentrations. Naturally occurring aluminum and iron were found in high concentrations. Residual pesticides were generally not detected in water but were detected in stream and reservoir sediments.

Key Words: Impoundment, Water, Sediment, Watershed, Pesticide, Herbicide, Insecticide, Metal

## INTRODUCTION

### Flood Control Reservoirs

There are nearly 80,000 substantial reservoirs constructed within the continental United States Concerns

about reservoir water and sediment quality are increasingly common as many of these reservoirs reach the end of their life-expectancy and are considered for de-commissioning or over-haul. During the 20th century, rapid increases in U.S. population, economy and technology spurred water control projects through-

out the nation Over half of existing U.S. dams were built during the period from 1945 to 1975, and the average age of U.S. reservoirs is 40 years. This suggests the need for greater dam maintenance and/or major rehabilitation [U.S. Army Corps of Engineers (USACE) 2000]. The National Performance of Dams Program (NPDP 2000) estimated that dam safety costs over the next 20 years could range from \$750 million to \$1.5 billion due to loss of capacity from sedimentation. Mitigation of potential aquatic life use and environmental and human health impacts from reservoir sediments and waters could result in exponential increases above dam safety costs. A far more comprehensive knowledge of the quantity and quality of sediments within reservoirs is needed to address future management decisions. In this paper, we describe a study of one large reservoir, addressing questions of upstream influence and sedimentation, sediment quantity and quality within the reservoir, and associated reservoir water quality.

### Yalobusha River Watershed and Grenada Reservoir

The U.S. Army Corps of Engineers (USACE) completed Grenada Reservoir, located in Grenada County, MS, in 1954. It is one of 555 reservoirs operated by the USACE out of approximately 2000 reservoirs controlled by the U.S. federal government (USACE 2000). Built primarily for flood control, the reservoir also serves for recreational activities, including swimming, fishing, and boating. It is one of over 3,300 reservoirs within the State of Mississippi referenced in the National Inventory of Dams (USACE 2000). Maximum storage capacity of Grenada Reservoir is approximately 3.33 trillion cubic meters (2.7 million acre-feet), about one tenth the capacity of the largest U.S. reservoir, Lake Mead, Nevada. Water level in Grenada Reservoir is controlled by outlet gates and normal elevation (National Geodetic Vertical Datum - NGVD) ranges from 59 m (193 ft) NGVD (40 km2 or 9,800 acres of water) to a maximum flood control elevation of 70 m (231 ft) NGVD (261 km2 or 64,600 acres of water). Water level is held at a recreational pool level of 65 m (215 ft) NGVD (145 km2 or 35,820 acres of water) during the summer months. The reservoir's flood control purpose requires a summer/fall season drawdown so that it will have maximum capacity for winter/ spring rains (annual precipitation may exceed 140 cm).

Two rivers provide inflow into the reservoir (Figure 1), the Yalobusha to the south, and the Skuna to the north, creating a distinctive Y-shaped reservoir with two large lateral arms to the east and the main body westward. Flow within the watershed and the reservoir

is from east to west, with controlled outflow from the reservoir into the Yalobusha River channel below the dam. Flow ultimately joins the Mississippi River along the western border of Mississippi via the Yazoo River that drains most of the northwestern region of the State. The contributing watersheds associated with the two river drainages (Fig. 1) differ in that the Yalobusha River watershed has a floodplain area of intensive agriculture, including large-scale production of sweet potatoes [Ipomoea batatus (L.) Lam.] rotated with cotton (Gossypium hirsutum L.), soybeans [Glycine max (L.) Merr.] and corn (Zea mays L). centered around the towns of Calhoun City and Vardaman, while the Skuna River watershed is currently less agricultural and more silvicultural.

The entire Grenada Reservoir watershed has been impacted by channelization projects and additional channel incision that began in the early 1900s. With the exception of approximately 21 kilometers (13 miles) in the Yalobusha River upstream of Grenada Reservoir, all of the river and major tributaries of the watershed have been channelized. Original channelization projects were conducted during the 1910s and 1920s. Repeated additional works were conducted in the late 1930s to 1950s when the Yalobusha River and Topashaw Creek, the major river tributary, became plugged with debris and sediment. Late in the 1960s the U.S. Department of Agriculture Soil Conservation Service began the last major series of watershed modifications above the reservoir including extensive clearing and dredging of many channels, and installation of numerous gully erosion control structures. Also during the 1960s some dredging was done in the upper reservoir, but the extent is unknown. A major cycle of channel incision, a response to previous channelization efforts, is currently migrating up watershed streams (Simon and Thomas 2002).

Also, over the past decade, an occlusive debris jam has formed in the Yalobusha River upstream of the non-channelized portion of the river east of the reservoir (Figure 1). This debris jam, in excess of 2 km long and formed from eroded upstream materials, is forcing river flow into adjacent riparian floodplain bottomland forest and, occasionally, agricultural fields and homes. The U.S. Army Corps of Engineers, under direction from Congress, is currently addressing this and other problems in the watershed through a system-wide approach. Tributary stabilization projects have already been enacted, and possible downstream (river and debris jam) actions are being studied and discussed.

alobusha

River

**Debris Jam Location** 

contaminants likely to occur, given the historical and

current land use (Tables 1, 2, 3). Samples from 26

stream/river locations within the Yalobusha River

watershed were taken around November 1 during 1996,

1997 and 1999 from mid water-column and the upper

10 cm of sediments. Additional water column samples

were taken from 13 of these sites on ten dates between

July 1997 and April 2002. Added sediment samples

Reservoir

69 21

2,791 61 12,498.57

13,998.57

24,851.79

59,461.43

12,219,000.00

were taken from six sites during January 2002.

**SEDIMENT** 

Debris Jam

11.18 1,664.50

5,500.00

14,750.00

7,250.00

28,562 50

14,437,500 00

18,509,857.14

Figure I. Grenada Reservoir system, including Grenada Reservoir, Yalobusha River Watershed (South) and the Skuna River

Table 1. Mean concentration ( $\mu g L^{-1}$ ) of eight metals in watershed components of the Yalobusha

Watershed

45.09

2,981 96

11,306 27

5,510.00

26,119.09

15,448 82

1,802,799.41

13,862,500.00

Skuna River

Grenada

Reservoir

METHODS AND MATERIALS

Mercury

Arsenic

Copper

Lead

Zinc

Chromium

Aluminum

Iron3,667.65

Kilometers

Watershed (North), with sampling locations indicated by rectangles.

River and Grenada Reservoir. ND = not detected.

Reservoir

4.13

20 00

3.14

8 19

21.86

2,259.57

8,250,437.50

ND

WATER

Watershed

0.01

2.75

2.23

3 21

1468

58.30

3,595 31

1,790 57

Sample collection and storage were done according to

suggested American Public Health Association

(Greenberg et al. 1992) methods. Samples were collec-

ted from overlying water and bottom sediment into

properly cleaned and solvent-rinsed glass sample

Sci,

the

containers. Analyses included concentration determinations for up to 8 metals and 48 pesticides or priority

Table 2. Mean concentration ( $\mu g L^{-1}$ ) of 25 priority pollutant pesticides and PCBs in watershed components of the Yalobusha River and Grenada Reservoir. ND = not detected.

	WATER		SEDIMENT		
	Watershed	Reservoir	Watershed	Debris Jam	Reservoir
Arochlor 1016	Nd	Nd	Nd	Nd	Nd
Arochlor 1221	Nd	Nd	Nd	Nd	Nd
Arochlor 1232	Nd	Nd	Nd	Nd	Nd
Arochlor 1242	Nd	Nd	Nd	Nd	Nd
Arochlor 1248	Nd	Nd	Nd	Nd	Nd
Arochlor 1254	Nd	Nd	Nd	Nd	Nd
Arochlor 1260	Nd	Nd	Nd	Nd	Nd
BHC-alpha	Nd	Nd	0.68	Nd	Nd
BHC-beta	Nd	Nd	1.85	73.11	Nd
BHC-delta	Nd	Nd	1.45	1 55	Nd
BHC-gamma	Nd	Nd	0.39	4.10	Nd
Chlordane	Nd	Nd	Nd	Nd	Nd
Toxaphene	Nd	Nd	0.08	Nd	Nd
DDD 4,4'	Nd	Nd	4.20	10.14	0.44
DDE 4,4'	Nd	Nd	12 58	6.16	0 73
DDT 4,4'	Nd	Nd	0.37	4.07	12.20
Aldrin	< 0.01	Nd	19.94	4.11	Nd
Dieldrin	< 0.01	Nd	2.01	Nd	Nd
Endrin	Nd	Nd	0.26	Nd	9.37
Endrın aldehyde	Nd	Nd	0.03	Nd	1.75
Endosulfan I	Nd	Nd	0.07	Nd	0.22
Endosulfan II	< 0.01	Nd	1 73	1.91	Nd
Endosulfan sulfate	Nd	Nd	Nd	Nd	Nd
Heptachlor	< 0.01	Nd	0.55	1.34	2.53
Heptachlor epoxide	0.02	Nd	0.13	Nd	0.19

Sediment samples from Grenada Reservoir were taken at 9 locations between December 1998 and May 1999. At each site, sediment cores were taken with manual coring equipment from an anchored boat. Tencentimeter-diameter sediment cores were driven, lifted into a clean semi-tubular ruled trough, and divided into incremental 10-cm sections by depth from sediment surface for metals, pesticides, contaminants and cesiumdating analyses. One kg of sediment from each 10-cm depth increment was acquired for cesium dating. Surface sediments at seven of these sites were sampled again in November 1999 (two sites were inaccessible because of low water). Concomitant with sediment sampling in the reservoir, water samples from mid water-column were collected for metals, pesticides and contaminants analyses.

Sediment samples from within the debris jam occluding the Yalobusha River upstream of the reservoir were collected on March 22, 2001. A 5 cm diameter

stainless steel hand corer was used to collect samples from four transects spaced along the length of the jam. At each transect, sediment to a maximum depth of 0.3 m was collected at three evenly spaced locations across the width of the channel and composited into a single sample. Woody and other (anthropogenic) debris within the jam prevented collection of deeper sediments. Analyses conducted on these samples were for only the eight metals and 25 priority pollutant residual compounds.

Analyses for contaminants were conducted in part (Table 3) at the USDA-ARS National Sedimentation Laboratory using gas chromatographic methods (Bennett et al. 2000, Smith et al. 1995, 2001) with both method detection and level of quantification limits equal to or less than 0.1  $\mu$ g kg<sup>-1</sup>. Other analytes, including the 25 priority pollu-tants and all metals, were quantified at the University

Table 3. Mean concentration ( $\mu g L^{-1}$ ) of recent-use pesticides in watershed components of the Yalobusha River and Grenada Reservoir. ND = not detected. X = not tested

	WATER		SEDIMENT		
	Watershed	Reservoir	Watershed	Reservoir	
Aldıcarb	Nd	X	Nd	Х	
Cyfluthrin	0 03	X	< 0.01	X	
Deltamethrin	Nd	X	X	X	
Methoxychlor	Nd	X	0.09	X	
Metribuzin	Nd	X	X	X	
Mirex	X	X	X	X	
Norflurazon	0 02	X	0.66	X	
Tefluthrin	Nd	X	X	X	
Tralomethrin	0.05	X	Nd	X	
Fipronil Sulfone	< 0.01	0.01	Nd	Nd	
Fluometuron	Nd	Nd	1.38	Nd	
Pendimethalin	< 0.01	< 0.01	0.35	0.10	
Bifenthrin	0.01	0 01	0.19	0.21	
Cyhalothrin-lambda	0.01	0.01	0.96	0 44	
Fipronıl	< 0.01	Nd	Nd	0.46	
Chlorfenapyr	0.02	0 08	0.62	0.60	
Cyanazine	0.01	0 17	0.02	1.03	
Chlorpyrifos	< 0.01	< 0.01	0.02	8 62	
Trifluralin	< 0.01	0.04	Nd	18.46	
Methyl parathion	0.02	0 02	0.71	41.44	
Metolachlor	0.12	0.16	0.01	86.44	
Alachlor	0.02	Nd	1.46	106.79	
Atrazine	2 05	0.42	0.51	218 67	

of Louisiana Monroe Soil-Plant Analysis Laboratory using ASTM and USEPA approved methods. Priority pollutants in water and sediment were tested according to EPA method SW 846:8140 with a detection limit of 1  $\mu$ g kg<sup>-1</sup>. Methods and detection limits for metals analyses were as indicated in Table 5.

#### RESULTS

# Water Quality

Analysis of water collected from stream sites in the upper Yalobusha River watershed showed only 11.60% (373 of 3215 possible) detection of pesticide/PCB compounds in samples. The only non-metal compound found in average concentration greater than 1  $\mu$ g L<sup>1</sup> in watershed water samples was atrazine. Mean concentration was elevated due to higher concentrations in detections from storm-flow sample collections. Highest

mean concentrations for non-metal compounds in the Yalobusha River watershed water samples were atrazine  $(2.05 \ \mu g \ L^{-1})$ , metolachlor  $(0.12 \ \mu g \ L^{-1})$ , tralomethrin  $(0.05 \,\mu\mathrm{g}\,\mathrm{L}^{-1})$ , and cyfluthrin  $(0.038 \,\mu\mathrm{g}\,\mathrm{L}^{-1})$  with all other detections well below  $0.10 \,\mu g \, L^{-1}$ . Mean concentrations of metals observed from water samples within the Yalobusha River watershed were; mercury  $(0.01 \mu g L^{-1})$ , copper (2.23  $\mu$ g L<sup>-1</sup>), arsenic (2.74  $\mu$ g L<sup>-1</sup>), chromium  $(3.21 \,\mu g \,L^{-1})$ , lead  $(14.68 \,\mu g \,L^{-1})$ , and zinc  $(58.30 \,\mu g \,L^{-1})$ 1). Higher concentrations were observed for aluminum  $(3595 \,\mu g \, L^{-1})$  and iron  $(3667 \,\mu g \, L^{-1})$ .

Within Grenada Reservoir, mid-column reservoir water samples revealed only 15.71% of possible nonmetal contaminant detections. Again, the highest observed mean concentration of non-metal compounds was observed for atrazine  $(0.42 \,\mu\mathrm{g}\,\mathrm{L}^{-1})$ . Cyanazine (0.17) $\mu g L^{-1}$ ) and metolachlor (0.16  $\mu g L^{-1}$ ) were the only other compounds observed with mean concentra-tion greater than  $0.10 \mu g L^{-1}$ . Aluminum (2260  $\mu g L^{-1}$ ) and iron (1791  $\mu g L^{-1}$ ) still had the highest observed concentration of all measured metals but were nearly half of levels observed in the upper watershed (Table 1). Copper concentration in water within the reservoir, however, was nearly an order of magnitude greater (20  $\mu g \ L^{-1}$ ) than in the watershed (2.23  $\mu g \ L^{-1}$ ). Arsenic (4.13  $\mu g \ L^{-1}$ ) had a mean concentration somewhat higher than observed in upper watershed streams (2.74  $\mu g \ L^{-1}$ ). Chromium (3.14  $\mu g \ L^{-1}$ ) mean concentrations were similar to watershed levels, while lead (8.19  $\mu g \ L^{-1}$ ) and zinc (21.86  $\mu g \ L^{-1}$ ) were approximately half of contributing watershed stream mean concentrations. Mid-column reservoir water samples never revealed presence of mercury.

## **Sediment Quality**

Analysis for non-metal contaminants within the upper Yalobusha River watershed stream drainage revealed only 11.64% of possible detections (N=1667) in sediments (Table 4). While this small percentage of detections was observed, nine compounds had mean concentrations greater than 1 µg L<sup>-1</sup>. Aldrin had a mean concentration of 19.95  $\mu$ g L<sup>1</sup> in sediment, but this was attributable to high concentrations of 3 samples in the depositional area upstream of the debris jam following a 1996 storm event. DDT  $(0.37 \,\mu g \,L^{-1})$ , DDE  $(12.58 \,\mu g \,L^{-1})$  $L^{-1}$ ) and DDD (4.20  $\mu$ g  $L^{-1}$ ) were present in low concentrations (Table 2) in stream and reservoir sediments; they were not detected in water. Dieldrin (2.01  $\mu$ g L<sup>-1</sup>), beta-BHC (1.85  $\mu g L^{-1}$ ), endosulfan II (1.73  $\mu g L^{-1}$ ), alachlor (1.46  $\mu$ g L<sup>-1</sup>), delta-BHC (1.45  $\mu$ g L<sup>-1</sup>), and fluometuron (1.38  $\mu$ g L<sup>-1</sup>) all had mean observed concentrations greater than 1 µg L<sup>-1</sup> in stream sediments, and 21 other non-metal contaminants were detected at lower levels. Mean concentrations of metals observed in watershed stream sediments ranged from lowest for mercury (45.09  $\mu$ g L<sup>1</sup>), to arsenic (2982  $\mu$ g L<sup>1</sup>), chromium (5510  $\mu$ g L<sup>1</sup>), copper (11306  $\mu$ g L<sup>1</sup>), zinc (15449  $\mu$ g L<sup>1</sup>), lead (26119  $\mu$ g L<sup>1</sup>), aluminum  $(1.80 \times 10^6 \mu g L^{-1})$  and iron  $(8.25 \times 10^6 \mu g L^{-1})$ .

Table 4. Detections of pesticides and PCBs in watershed components of the Yalobusha River (YR) and Grenada Reservoir (GR).

	Water		Sediment	
	YR	GR	YR	GR
Number of Detections	373	74	194	121
Number Possible	3215	47 I	1667	801
Detection Rate (%)	11.60	15 71	11.64	15,11

Table 5. Methods used and method detection limits (MDL) for quantifying metal concentrations during this study. Information for pesticides is given in the text.

Analysis	Method	MDL ( $\mu$ g L <sup>-1</sup> or $\mu$ g kg <sup>-1</sup> )
Mercury	EPA 245.1	0 1
Arsenic	EPA 206.2	1
Copper	EPA 200.7	3
Chromium	EPA 200.7	2
Lead	EPA 200.7	15
Zinc	EPA 200.7	3
Aluminum	EPA 200 7	60
Iron	EPA 200.7	2

Yalobusha River debris jam samples, as all other samples collected for this study, did not contain any arochlor PCB compounds. Debris jam sediments did harbor some DDT and BHC, in concentrations higher than observed in upper stream sediments (Table 2). Of the other residual analytes, only aldrin (4.11  $\mu$ g L¹), endosulfan II (1.91  $\mu$ g L¹), and heptachlor (1.34  $\mu$ g L¹) were detected Less mercury, arsenic, copper and lead were found in debris jam sediments than in watershed streams or reservoir sediments. Chromium and aluminum sediment concentrations in the jam were similar to those of reservoir sediments, while zinc and iron in the jam were intermediate between sediment concentration levels of watershed streams and Grenada Reservoir (Table 1).

Reservoir sediments had the highest overall mean pesticide concentrations of watershed components tested and a detection rate of 15.11% (121 of 801 possible). Within Grenada Reservoir, atrazine was found in greatest observed levels, with a mean concentration of 218.7  $\mu$ g L<sup>-1</sup>. The herbicides alachlor (106.8)  $\mu g L^{-1}$ ) and metolachlor (86.44  $\mu g L^{-1}$ ) were also observed at high mean concentrations; however, alachlor was widely distributed within the reservoir while metolachlor was detected at only two sites. Methyl parathion (41.44  $\mu$ g L<sup>-1</sup>) and trifluralin (18.46)  $\mu g L^{-1}$ ) were widely distributed among sampling sites. Chlorpyrifos (8.62  $\mu$ g L<sup>-1</sup>) was observed only at 2 sites, while  $\Sigma$ DDT (13.33  $\mu$ g L<sup>-1</sup>) was observed throughout the reservoir. Four other pesticides had observable mean concentrations greater than I µg L-1 in reservoir sediments; endrin (9.37  $\mu$ g L<sup>-1</sup>), heptachlor (2.53  $\mu$ g L<sup>-1</sup>) ), endrin aldehyde (1.75  $\mu$ g L<sup>-1</sup>) and cyanazine (1.03  $\mu$ g L<sup>-1</sup>) Ten other compounds were detected. Mean concentrations of arsenic (2792  $\mu$ g L<sup>-1</sup>), copper (12499  $\mu$ g L<sup>-1</sup>) and lead (24852  $\mu$ g L<sup>-1</sup>) observed in reservoir sediments were comparable to upper watershed concentrations. Mean mercury (69.21  $\mu$ g L<sup>-1</sup>), chromium (13999  $\mu$ g L<sup>-1</sup>) and iron (18.5 x 10<sup>6</sup>  $\mu$ g L<sup>-1</sup>) concentrations in reservoir sediments were approximately 1.5 to 2 times greater than observed for sediments in the upper watershed. Zinc (59461  $\mu$ g L<sup>-1</sup>) concentrations were found at about 4 times the mean level observed in the upper watershed stream sediments. Aluminum (12.2 x 10<sup>6</sup>  $\mu$ g L<sup>-1</sup>) mean reservoir sediment concentrations were about 7 times higher than observed in upper watershed samples.

### **Sedimentation Rates**

Sediment accumulation within the permanent pool adjacent to the dam was <1 cm yr<sup>-1</sup> except for a depositional area near a tributary inflow that accumulated sediment at about 5 cm yr<sup>-1</sup>. The central area of the permanent pool closer to river inflow experienced sediment accumulation rates that averaged < 1.5 cm yr<sup>-1</sup>. Sites proximal to the main reservoir body but within the two reservoir arms fed by the two river inflows showed practically no sedimentation, probably due to scouring action. Reservoir water level management practices result in annual (summer/fall) drawdown. Subsequent seasonal river inflow is constricted in these areas and may create underflow currents. Observed sedimentation rates further upstream where river water from the Yalobusha and Skuna rivers entered the reservoir were also generally low. Overall, sedimentation rates within Grenada Reservoir were higher from 1954 until the mid 1960's and early 1970's but were considerably lower thereafter. These lower sedimentation rates paralleled land use changes that reduced row-crop agricultural area and increased soil conservation measures. Lower sediment accumulation also followed discontinuation of major upstream channel alterations aimed at flood control in the river floodplain. In recent years, a large debris jam has blocked the main river channel (Simon and Thomas 2002) and forced flood flows into adjacent floodplain wetlands where much sediment has been deposited.

### DISCUSSION

Most pesticides were detected seasonally at low concentrations in contributing streams. The 48 pesticides/contaminants (excluding metals) that we tested showed a maximum occurrence detection of 15.71%. PCBs (arochlor compounds) were not observed

in any medium (water or sediment) or location (watershed stream or reservoir) sampled during this project. Reservoir mid-column-depth water samples never yielded detections of pesticides in concentrations greater than 1.0  $\mu$ g L<sup>-1</sup>; and legacy residual pesticides were never detected at any concentration in reservoir water samples. Surface water contaminants that were detected in the watershed streams at greater than  $1.0 \mu g$ L<sup>-1</sup> included only recently used chemicals (atrazine 13) detections, metolachlor 3 detections, and cyfluthrin 1 detection). Compounds found in surface water were almost exclusively these recent pesticides that are more water-soluble than older residual compounds that were often found in the stream sediments. Detections of watershed stream sediment contaminants in concentrations greater than 1.0  $\mu$ g L<sup>-1</sup> (9 compounds) were observed for a variety of both current-use and residual pesticides, with 30 total compounds detected. Reservoir sediments also contained both residual and current-use pesticides (20 compounds) Slightly more current-use pesticides (14 compounds) were detected in sediments of streams than were detected in the reservoir (12 compounds). Only 8 of 25 residual pollutants were detected in reservoir sediment samples, while twice that number, 16, were detected in stream sediments.

Atrazine, a common broadleaf and grass herbicide used in corn production, was the only current use pesticide found in significant concentrations in streams draining into Grenada Reservoir. Atrazine was also detected in reservoir water, but at nearly one fifth less than contributing stream concentrations. However, concentrations were higher in reservoir sediments. Atrazine has been previously shown to be a widely detected contaminant of streams and rivers in the Midwestern U.S., particularly following high-flow runoff events (Council on Environmental Quality 1993) and, as shown by our results, can accumulate in reservoir sediments; detection rate was 39%. Atrazine is practically nontoxic to birds. The LD50 is greater than 2000 mg kg<sup>-1</sup> in mallard ducks. At dietary doses of 5000 mg kg-1 in toxicity studies, no effect was observed in bobwhite quail and ring-necked pheasants (U.S. National Library of Medicine 1995). Atrazine is slightly toxic to fish and other aquatic life. It has a low level of bioaccumulation in fish. In whitefish, atrazine accumulates in the brain, gall bladder, liver, and gut (U.S. National Library of Medicine 1995). Stream water contained a mean of 2.05  $\mu$ g L<sup>-1</sup>; reservoir water contained an order of magnitude less atrazine (mean=  $0.42 \mu g L^{-1}$ ). Attrazine is highly persistent in soil. Because it does not adsorb strongly to soil particles and has a lengthy half-life (60 to greater than 100 days), it has a high potential for groundwater contamination

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despite its moderate solubility in water (Wauchope et al. 1992)

We detected alachlor, a grass and broadleaf weed herbicide commonly used in soybeans and corn, at mean concentrations of  $106.79 \mu g L^{-1}$  in reservoir sediment but only  $0.02 \,\mu\mathrm{g}\,\mathrm{L}^{-1}$  in stream water and 1.46 $\mu g L^{-1}$  in stream sediment; it was not detected in reservoir water. Alachlor is practically nontoxic to wildfowl Alachlor has a 5-day dietary LC<sub>50</sub> of greater than 5000 mg kg<sup>-1</sup> in young mallards and bobwhite quail (Weed Science Society of America 1994). It is moderately toxic to fish at levels much higher than we detected. The LC<sub>50</sub> (96-hour) for alachlor is 2.4 mg L<sup>-1</sup> in rainbow trout, 4.3 mg L<sup>-1</sup> in bluegill sunfish, 6.5 mg L<sup>-1</sup> in catfish, and 4.6 mg L<sup>-1</sup> in carp (U.S. National Library of Medicine 1995). It is slightly toxic to crayfish, with a LC<sub>50</sub> (96-hour) of 19.5 mg L<sup>-1</sup>. The bioaccumulation factor in channel catfish is 5.8 times the ambient water concentration, indicating that alachlor is not expected to accumulate appreciably in aquatic organisms (U.S. National Library of Medicine 1995).

We detected the herbicide metolachlor in watershed stream water (0.12  $\mu$ g L<sup>-1</sup>) and stream sediment  $(0.01 \mu g L^{-1})$  and reservoir water  $(0.16 \mu g L^{-1})$  and sediments (86.44  $\mu$ g L<sup>-1</sup>). Metolachlor is also practically nontoxic to birds. The reported oral  $LD_{50}$  is greater than 2000 mg kg<sup>-1</sup> in mallard ducks and is greater than 4500 mg kg<sup>-1</sup> in bobwhite quail (Weed Science Society of America 1994). Metolachlor is moderately toxic to both cold- and warm water fish, including rainbow trout, carp, and bluegill sunfish. Reported 96-hour LC<sub>50</sub> values for this compound are about 3 mg L<sup>-1</sup> in rainbow trout, 5 mg L<sup>-1</sup> in carp and channel catfish, and 15.0 mg L<sup>-1</sup> in bluegill sunfish (Weed Science Society of America 1994). Metolachlor is moderately persistent in the soil environment. In a study involving 14 states, it was also found in a number of surface water samples at a maximum concentration of 0.138 mg L<sup>-1</sup> (Howard 1991). These levels probably result from runoff during spring and summer applications to fields. Metolachlor is highly persistent in water over a wide range of acidity. Its half-life at 20° C is more than 200 days in highly acid waters, and is 97 days in highly basic waters. Waters sampled in this study were generally acidic.

Cyfluthrin, a synthetic pyrethroid used in all 4 major watershed crops, was found in water and sediment of streams only. It is of low toxicity to upland game birds and waterfowl.  $LD_{50}$  values range from greater than 2,000 mg kg<sup>-1</sup> in acute oral tests with bobwhite quail, to greater than 5,000 mg kg<sup>-1</sup> in subacute tests with both mallards and bobwhite quail (U.S. EPA 1987). As is the normal case with pyrethroids,

cyfluthrin is highly toxic to freshwater organisms. The concentration of cyfluthrin in water that resulted in the mortality of half of the test organisms (LC<sub>50</sub>) was 0.68  $\mu$ g L<sup>-1</sup> in rainbow trout, 0.0015 mg L<sup>-1</sup> in bluegill, and 0.022 mg L<sup>-1</sup> in carp (U.S. EPA 1987) Cyfluthrin is exceptionally toxic to the freshwater invertebrate *Daphnia magna*, (LC<sub>50</sub> = 0.14 ng L<sup>-1</sup>). The LC50 for the sheepshead minnow was 4  $\mu$ mg L<sup>-1</sup> (U.S. EPA 1987).

Chlorfenapyr was detected at low concentrations in water and sediment from both the watershed streams and reservoir. Chlorfenapyr is an insecticide that was applied only under one-time application permission for cotton in the 1990s. It was never fully registered because of its toxicity. While it is slightly to highly toxic to mammals, chlorfenapyr is highly to very highly toxic to birds, and is very highly toxic to all aquatic organisms for which data was submitted (U.S.EPA 1998).

Fluometuron, a current use herbicide with a very low toxicity was also present in watershed sediments  $(1.38 \,\mu g \, L^{-1})$ . It was not detected in water or reservoir sediments. Fluometuron is practically nontoxic to birds; the reported acute oral LD<sub>50</sub> values for fluometuron are greater than 2150 mg kg<sup>-1</sup> in bobwhite quail and 2974 mg kg<sup>-1</sup> in mallards (Weed Science Society of America 1994). Fluometuron is only slightly toxic to fish The reported 96-hour LC<sub>50</sub> of technical fluometuron is 30 mg L<sup>1</sup> in rainbow trout, 48 mg L<sup>1</sup> in bluegill sunfish, 170 mg L<sup>-1</sup> in carp, and 55 mg L<sup>-1</sup> in catfish. In catfish, tissue concentrations in whole fish were 40 times that of the ambient water, indicating low capacity for bioaccumulation (U.S. National Library of Medicine 1995) The reported 48-hour LC<sub>50</sub> for fluometuron in Daphnia (water flea) is 54 mg L<sup>-1</sup> (Weed Science Society of America 1994), indicating slight toxicity to aquatic invertebrates.

Aldrin and dieldrin were found in watershed stream sediments after significant watershed runoff events (October, 1996, November, 1999; January, 2002) Aldrin breaks down to dieldrin naturally in the environment. From 1950 to 1970, aldrin and dieldrin were popular pesticides for corn and cotton. Because of concerns about damage to the environment and the potential harm to human health, EPA banned aldrin and dieldrin in 1974 except for control of termites. In 1987, EPA banned all uses (ATSDR 2000). Neither of these compounds were detected in water or sediments in Grenada Reservoir.

We found several other banned, residual insecticides in watershed sediments, but they were not generally present in surface water in the watershed streams, and none were found in reservoir water. Residual contamination from DDT was detected in low

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concentrations, most consistently in reservoir sediments The Mississippi Department of Environmental Quality has a fish flesh advisory (Randy Reed, personal communication) that recommends limited consumption of fish flesh that contains greater than 1.0 mg kg<sup>-1</sup> of  $\Sigma$ DDT. If bioaccumulation increased concentrations in fish by up to one order of magnitude above water or sediment (Cooper 1991, Knight and Cooper 1996), fish flesh values would not be excessive. Our observations corresponded to national findings. While nation-wide advisories against fish consumption due to mercury and PCB more than doubled for the U.S. from 1993 to 1998, cases due to dioxin and chlordane have remained level and those because of DDT have declined as pastuse pesticides slowly degrade (U.S. EPA 1999).

Naturally occurring metals were found in high concentrations, particularly aluminum and iron. Stream or reservoir water generally contained three orders of magnitude lower concentrations of metals than did underlying sediments. Chromium concentrations in both watershed streams and in Grenada Reservoir were within acceptable limits (mean=3.5  $\mu$ g L<sup>-1</sup>; 3.1  $\mu$ g L<sup>-1</sup>) although larger amounts accumulated in some watershed stream sediments. U.S. EPA has set a limit of 100  $\mu$ g chromium (III) and chromium (VI) per liter of drinking water (100  $\mu$ g L<sup>-1</sup>) (ATSDR 2000).

Spikes of concentrations caused an elevated mean in many contaminants. These spikes were generally associated with intensive rainfall events that eroded soil from source fields. Residual compounds that adhered to eroding soil particles migrated downstream with watershed sediment. As this material moved into the stagnant river region above the Yalobusha River debris jam and out into the adjacent floodplain in recent years, much of it was deposited. Our detection of fewer residual contaminant compounds in the debris jam surface sediments (than in upstream sediments) indicates the possibility that accelerated breakdown (at least for some compounds) is occurring atop the jam as sediments are exposed to sunlight and air and that leaching during high water and concomitant resuspension of clay particles occur. Sand-sized sediment in the jam also reduced concentrations of contaminants below concentrations that would have been observed with clay sediments. The presence of the jam has temporarily reduced the amount of contaminants available to be detected in recent reservoir sediments. The percent reduction is unknown. Future study of the debris jam and surrounding floodplain sediments should increase our understanding of the processes occurring there and effects on Grenada Reservoir sediment and water quality.

Watershed use has had a measurable effect on

reservoir sediment accumulation During the 1950's and 60's when tillage was more intensive and channelization projects were being undertaken in the watershed, sediment accumulation was greater in Grenada Reservoir than in more recent times. In spite of continuing erosion problems in the watershed, sediment accumulation does not present immediate threats to reservoir storage. Accumulating sediments are not presently creating significant water quality difficulties.

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